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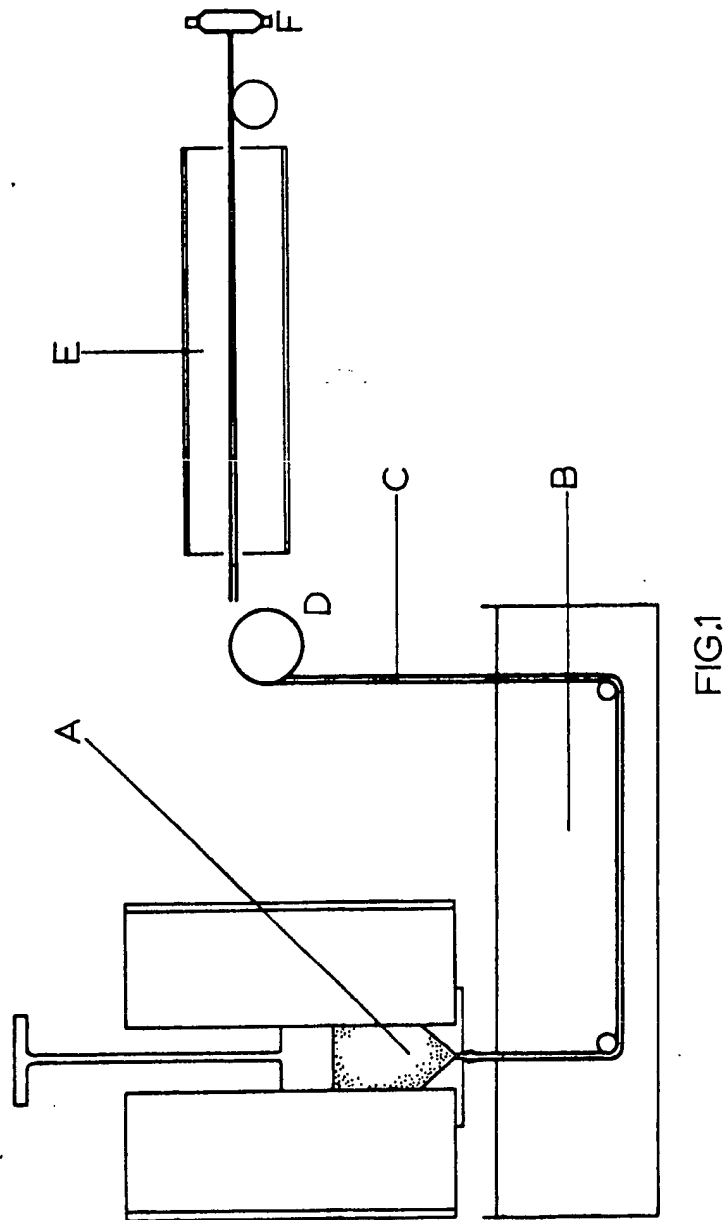
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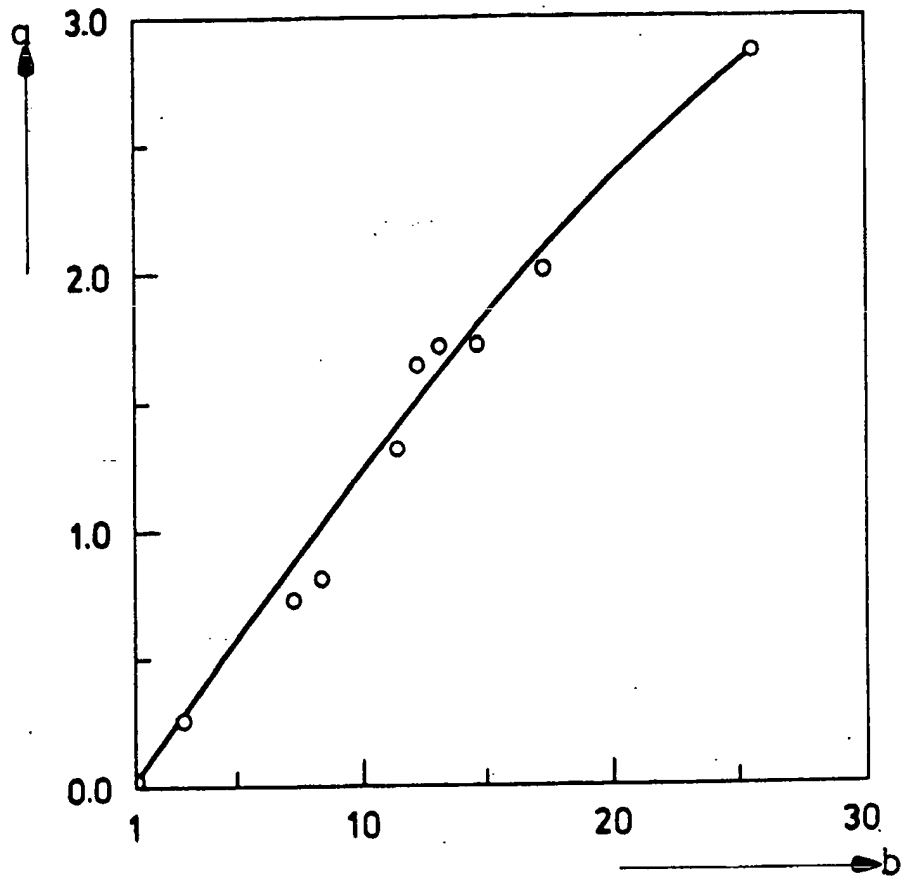
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(54) Dry-spinning polymer filaments

(57) A process for making polymer filaments which have a high tensile strength and a high modulus by stretching a polymer filament which contains a substantial amount, eg at least 25 wt % of polymer solvent at a temperature between the swelling point and the melting point of the polymer. A solution of the polymer may be spun to a filament through a spinning aperture and the spun filament cooled to below the dissolution temperature of the polymer without substantial evaporation of solvent from the filament and then brought to a temperature between the swelling point and the melting point of the polymer, and stretched. By the process polyethylene filaments may be obtained having a tensile strength of at least 1.2 GPa.

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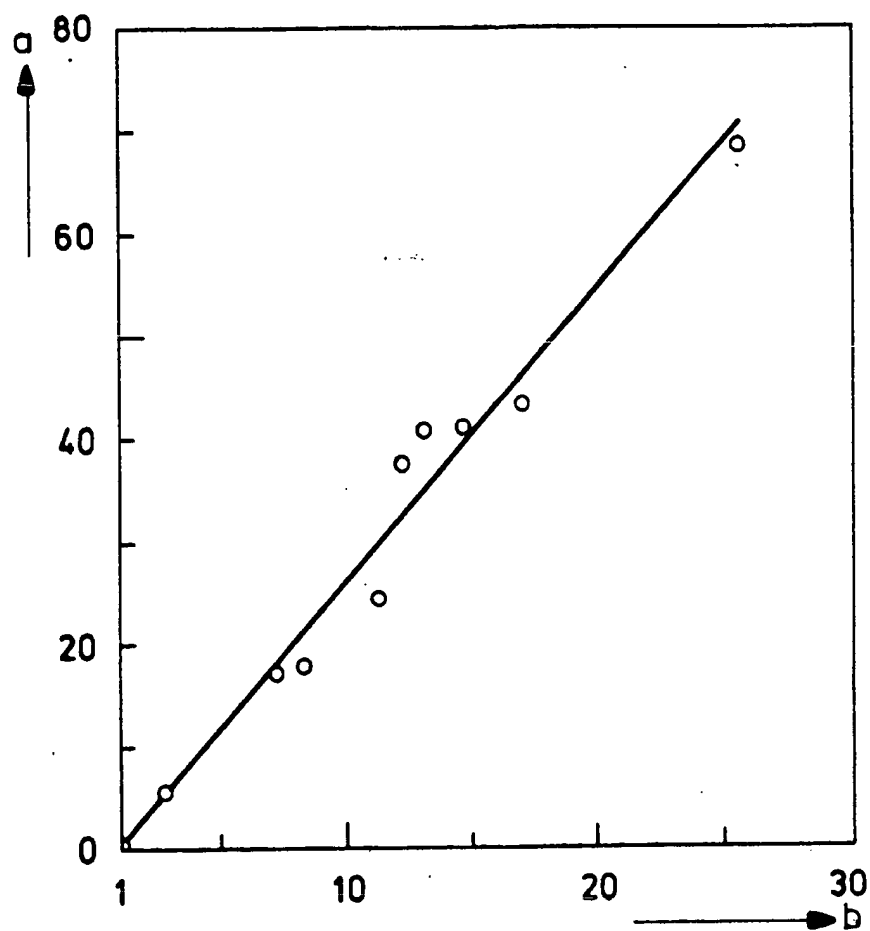


FIG.3

SPECIFICATION

Filaments of high tensile strength and modulus

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This invention relates to polymer filaments of high tensile strength and modulus, and to a process of making such filaments by spinning a solution of spinnable polymer material.

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Filaments are made by spinning linear polymers in liquid form, i.e. as a melt or solution. The randomly oriented chains of molecules in the filament thus obtained are then oriented lengthwise in the filament by stretching. Although also other substances may be capable of being spun, the chain-formed macromolecules are an important condition of their capability of being spun into filaments. Side branches have an adverse effect on filament formation and mechanical properties. Therefore the production of polymer filaments utilizes polymers that are substantially linear, although a limited degree of branching will in most cases be unavoidable, and allowable.

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By stretching the filaments, the chain macromolecules are oriented lengthwise and the strength of the filaments increases. However in many instances the strength remains far below the value that is theoretically possible.

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Many attempts have previously been made at producing filaments the tensile strength and modulus of which come closer to what is theoretically possible, as described in the publication by Juyn in *Plastica* 31 (1978)

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262-270 and Bigg in *Polymer Eng. Sci.* 16 (1976) 725-734 and have failed to yield satisfactory results. In a number of instances it was possible to sufficiently improve the modulus but not the tensile strength, but the filament formation is so slow that economic production is impossible.

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It has now been found that polymer filaments of high tensile strength and modulus can be made by stretching a polymer filament containing a substantial proportion of polymer solvent, at a temperature between the swelling point and the melting point. Preferably a solution of a spinnable polymer is spun through a spinning aperture and the spun filament is cooled below the dissolution temperature of the polymer without substantial evaporation of solvent from the filament and is then heated to a temperature between the swelling point of the polymer in the solvent and the melting point of the polymer, and is stretched.

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In the process called dry spinning, a generally known process applied on a technical scale, a solution of a spinnable polymer is spun in a shaft through which—usually heated—air is blown to evaporate all or most of the solvent from the filament. The temperature in the shaft is below the melting point of the polymer, so that this is precipitated when the solvent is evaporated. This increases the

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mechanical strength of the filament, which is still very low at the exit through the spinning aperture. The strength is further increased in the following stretching operation at temperatures below the melting point of the polymer.

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According to the present invention, the evaporation of the solvent from the filament immediately after spinning is not promoted during the cooling phase. The filament can be cooled to below the solution temperature, and particularly to below the swelling point of the polymer in the solvent, in any suitable way, for instance by passing the filament into a water bath, or through a shaft, with no or hardly any air being blown through this shaft. Some evaporation of the solvent from the filament will often take place spontaneously and not be preventable. This does not do the least harm, as long as the evaporation is not actively promoted and the amount of solvent in the filament is not reduced to a low value, e.g. to less than 25% by wt. of solvent relative to the polymer, preferably not to less than equal amounts (100%) by weight of solvent and polymer. If so desired, evaporation of the solvent may be reduced or suppressed by carrying out the spinning in an atmosphere containing solvent vapour.

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In cooling to below the solution temperature, in particular to below the swelling temperature of the polymer in the solvent, the polymer precipitates from the solution, and a gel is formed. A filament consisting of this polymer gel has sufficient mechanical strength for further processing, e.g. by means of the guides, rolls, etc., customarily used in spinning techniques. A filament of this kind is heated to a temperature between the swelling point of the filament in the solvent and the melting point of the polymer, and stretched at that temperature. This can be effected by passing the filament into a zone containing a gaseous or liquid medium kept at the required temperature. A tubular oven with air for the gaseous medium is very suitable, but it is also possible to use a liquid bath or any other suitable device. A gaseous medium is easier to handle, and deserves preference.

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When the filament is being stretched, solvent evaporation, or—if a liquid medium is used—dissolution of solvent in the liquid will occur. By preference, evaporation is promoted by adequate measures, e.g. removal of the solvent vapour, for instance by leading a gas or air current past the filament in the stretching zone. At least part of the solvent should be evaporated, but by preference at least the greater part of the solvent is evaporated, so that at the end of the stretching zone at most a small amount—e.g. not more than a few per cent, calculated on a solid-substance basis—of solvent is contained in the filament. The filament eventually obtained must be free of solvent, and it is advantageous to apply such conditions that it is free, or virtually free, of

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solvent already in the stretching zone.

Surprisingly, the process according to the invention can produce filaments that are considerably stronger than filaments of the same material made by any of the usual dry spinning processes, that is to say, filaments of considerably higher tensile strength and modulus. By means of the methods described in the abovementioned publications by Juyn and Bigg filaments of higher modulus have been made, admittedly, but the tensile strength still leaves much to be desired. Moreover, the productivity of these methods is low.

The process according to the invention differs from the usual dry spinning processes in that a filament containing an appreciable amount of solvent for the spinnable material is stretched at a temperature at which the spinnable material will at least swell in the solvent, with removal of the solvent, whereas in the usually applied spinning processes solvent-free filaments are subjected to stretching.

A requirement of dry spinning is that the linear polymer be soluble in a suitable solvent. For any soluble polymer a number of solvents are known. The expert can without any difficulty select therefrom a suitable solvent whose boiling point is not so high as to make it difficult for the solvent to be evaporated from the filament, and not so low as to make it too volatile and hinder filament formation on account of rapid evaporation, or has to be used under pressure to prevent this.

Dissolution of a polymer in a suitable solvent involves swelling. Whilst solvent is absorbed and the volume increases, a strongly swollen gel is formed, which however, on account of its consistency and stability of shape still has to be regarded as a kind of solid substance. It is generally assumed that the polymer is composed of ordered (crystalline) and less ordered (amorphous) area. The ordered areas are believed to act as anchoring points and thus lend stability of shape to the gel. The formation of the gel and the dissolution are time-dependent. A given polymer can be dissolved in a given solvent only above a given temperature. Below this dissolution temperature only swelling takes place, and according as the temperature is lower, the swelling becomes less, until at a certain point it is negligible. The swelling point or swelling temperature is considered to be that temperature at which a distinct increase in volume and a distinct absorption of solvent—5 to 10% of the polymer weight—occur. For the sake of simplicity, the swelling temperature above which the stretching is to be effected is the temperature at which 10% of solvent is unquestionably absorbed into the swelling polymer.

In dry spinning processes as usually applied, mostly 5–30% wt. solutions are used, for technical and economic reasons. Such solutions are suitable also for the present

process, although in general use will be made of solutions of lower concentration. Advantageously, use is made of 1–5% wt. solutions. Still lower concentrations can sometimes be applied, although these do not present advantages and are economically disadvantageous.

Suitable stretching ratios can be easily determined by experiment. Tensile strength and modulus of the filaments are, within certain limits, about proportional to the stretching ratio. According as the filaments should be stronger, a greater stretching ratio will have to be chosen.

The stretching ratio is at least 5, by preference at least 10, more in particular at least 20. High stretching ratios, 30 to 40 and even higher, can be applied without objection, and give filaments whose tensile strength and modulus are appreciably higher than those of filaments made by the usual processes.

In dry spinning processes as usually applied, the diameters of the spinning apertures in the spinning nozzles are usually small. In general, these diameters are 0.02–1.0 mm. Especially if small spinning apertures (≤ 0.2 mm) are used, the spinning process proves highly sensitive to the presence of impurities in the spinning solution, so that this should be carefully freed and kept free of solid impurities. In most cases, filters are placed on the spinning nozzles. In spite of this, it appears that the spinning nozzles need to be cleaned after a short time, and blockage still occurs frequently. In the present process larger spinning apertures, of more than 0.2 mm, e.g. 0.5 to 2.0 mm or more, can be used, since considerably higher stretching ratios can be applied and, in addition, generally lower polymer concentrations in the spinning solution are applied.

The invention is not restricted to the production of strong filaments of certain polymers, but can be generally used for materials that can be dry-spun to filaments.

Polymers that can be spun by the process according to the present invention are, for instance, polyolefins such as polyethylene, polypropylene, ethylene-propylene copolymers, polyoxymethylene, polyethylene oxide, polyamides, such as the various types of nylon, polyesters, such as polyethyleneterephthalate, polyacrylonitrile, vinyl polymers such as polyvinylalcohol, polyvinylidene fluoride.

Polyolefins such as polyethylene, polypropylene, ethylenepropylene copolymers and higher polyolefins can without objection be dissolved in hydrocarbons such as saturated aliphatic and cyclic, as well as aromatic hydrocarbons, or mixtures thereof such as mineral oil fractions. Very suitable are aliphatic or cyclic hydrocarbons such as nonane, decane, undecane, dodecane, tetralin, decalin, etc., or mineral oil fractions corresponding in boiling range. Polyethylene or polypropylene is preferably dissolved in decalin or dodecane. The

present method is particularly suitable for the preparation of filaments of polyolefins, preferably polyethylene having a tensile strength of at least 1.2 GPa.

- 5 It is also possible to make filaments of solutions of two or more polymers in a common solvent by the present process. For this purpose the polymers need not be miscible with each other. For instance, it is possible to
10 dissolve together in decalin or dodecane polyethylene and polypropylene, whose melts are immiscible, and to spin the solutions thus obtained.

- The filaments according to the invention
15 can be used for many purposes. They can be applied as reinforcement in many kinds of materials for which reinforcement with fibres or filaments is known, for tyre yarns, and for all possible applications in which low weight
20 combined with high strength is a desirable feature. As a matter of course, the range of possible application is not limited to those mentioned above.

- The invention will be elucidated by means
25 of the following examples, without being restricted thereby.

Example 1

- A polyethylene of high molecular weight,
30 with $\bar{M}_w \approx 1.5 \times 10^6$, was dissolved in decalin at 145°C to form a 2% wt. solution. This solution A was spun through a spinning nozzle with a spinning aperture of 0.5 mm dia., at 130°C. The filament was passed into
35 a water bath B kept at room temperature, where it was cooled. The cooled, 0.7 mm thick filament C, which was gel-like in appearance and still contained about 98% solvent, was next passed over feed reel D through a
40 tubular oven E heated at 120°C, and stretched over stretching reel F, with the use of various stretching ratios. This process is shown in diagram in Fig. 1.

- Figs. 2 and 3 show, respectively, the tension strength and the modulus a plotted
45 against the stretching ratio b . A modulus of more than 60 GPa and a tensile strength of almost 3 can be attained, whereas the modulus of polyethylene filaments made in the
50 conventional way is 2–3 GPa, and the tensile strength about 0.1 GPa. The values of modulus and tensile strength of filaments made with different stretching ratios as plotted in
Figs. 2 and 3 are mentioned in Table 1.

- 55 Polyethylene filaments having a tensile strength of over 1.2 GPa can easily be produced by means of the present process.

Table 1

| Expt. | Stretching ratio | Modulus, GPa | Tensile strength GPa |
|-------|------------------|--------------|----------------------|
| 70 | | | |
| 1 | 1 | 2.4 | 0.09 |
| 2 | 3 | 5.4 | 0.27 |
| 3 | 7 | 17.0 | 0.73 |
| 4 | 8 | 17.6 | 0.81 |
| 75 | 5 | 11 | 23.9 |
| 6 | 12 | 37.5 | 1.65 |
| 7 | 13 | 40.9 | 1.72 |
| 8 | 15 | 41.0 | 1.72 |
| 9 | 17 | 43.1 | 2.11 |
| 80 | 10 | 25 | 69.0 |
| 11 | 32 | 90.2 | 3.02 |

Example 2

- According to the process described in Example 1, a 2% wt. solution of a mixture of
85 equal parts of high-molecular-weight polyethylene, with $\bar{M}_w \approx 1.5 \times 10^6$, and a high-molecular-weight polypropylene, with $\bar{M}_w \approx 3.0 \times 10^6$, was spun at 140°C and stretched at 130°C, using a stretching ratio of 20. The
90 filaments had a tensile strength of 1.5 GPa.

Example 3

- According to the process described in Example 1, a 2% wt. solution of isotactic polypropylene, with $\bar{M}_w \approx 3.0 \times 10^6$, was spun at
95 140°C and stretched at 130°C, using a stretching ratio of 20. The tensile strength of the resulting filaments was 1 GPa.

CLAIMS

1. A process for making polymer filaments of high tensile strength and modulus, characterized in that a polymer filament containing a
105 substantial proportion of solvent for the polymer is stretched at a temperature between the swelling point and the melting point of the polymer.

2. A process according to Claim 1, characterized in that a solution of the polymer is spun to a filament through a spinning aperture and the spun filament is cooled to below the dissolution temperature of the polymer without substantial evaporation of solvent from the filament and is then brought to a temperature between the swelling point and the melting point of the polymer, and is stretched.

3. A process according to Claim 2, wherein the cooled filament consisting of a polymer gel, is heated to a temperature between the swelling point of the polymer in the solvent and the melting point of the polymer and the thus-heated filament is stretched with
120 at least partial evaporation of the solvent.

4. A process according to Claim 2 or Claim 3, wherein the spun filament is cooled to below the swelling point, and then stretched at a temperature between the swelling
130 point and the melting temperature.

5. A process according to any of Claims 1 to 4, wherein from 1 to 5 wt. % polymer solution is spun and stretched.
6. A process according to any of Claims 1 to 5, wherein a filament containing at least 25% wt. solvent based on the polymer, is stretched.
7. A process according to Claim 6, wherein the said filament contains at least 100% wt. solvent based on the polymer.
8. A process according to any of Claims 1 to 7, wherein the stretching ratio is at least 5.
9. A process according to Claim 8, wherein the stretching ratio is at least 10.
10. A process according to Claim 1, substantially as hereinbefore described.
11. Filaments made by a process according to any of Claims 1 to 10.
12. Polyethylene filaments having a tensile strength of at least 1.2 GPa.